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Polarographic Determination of 8-Hydroxyquinolines after Extraction with Naphthalene. Trace Analysis of Cadmium and Lead

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A rapid extraction-polarographic method has been developed for the direct determination of cadmium and lead extracted into the organic phase. 8-Hydroxyquinolines of cadmium and lead were extracted with molten naphthalene in the pH range of 7–10 and 9–12 respectively; as the temperature was lowered, naphthalene separated out as a solid mass containing the metal-oxinate. This solid mass was dissolved in DMF and the polarograms were recorded using 0.1 M sodium perchlorate–0.1 M perchloric acid in case of cadmium and 0.1 M pyridine–0.1 M perchloric acid in case of lead as the supporting electrolytes. Under these conditions, these metal-oxinates gave well defined waves with $E_{1/2}$ of -0.63 V and -0.47 V *vs* SCE respectively. The relation between diffusion current and concentration is linear in the range of, 0.0–112 $\mu\text{g}/10$ ml for Cd and 0.0–207.0 $\mu\text{g}/10$ ml for Pb. The interferences of various ions had been studied in details; extraction was not possible in the presence of EDTA in both the cases and among the metal ions studied, no interference was noticed in case of cadmium while Pd, Cd and Hg(II) interfered in case of lead. The interference of these ions were eliminated with sodium cyanide. The method is so simple, rapid and sensitive that can be applied for the determination of these ions in various complex materials.

Part-1 Cadmium

Several heterocyclic nitrogen containing compounds are widely used as analytical reagents.¹⁾ Among these compounds, 8-hydroxyquinoline (oxine) is one of the most popular and versatile organic reagents which react at least with more than fifty elements. The studies of this reagent in solvent-extraction revealed that even with the proper control of pH, this reagent is not made selective in extracting specific elements although many masking agents have also been examined.²⁾ Use of this reagent in the analysis of some of the metals by the new technique; solid-liquid separation after liquid-liquid extraction and estimation of metals by spectrophotometric method have been reported from these laboratories.³⁾ On the other hand, a survey of the literature reveals that there are few polarographic methods for the direct determination of metals in the organic phase after extraction.^{4–7)} All these methods are involved with the use of mixed solvents *i.e.*; the extract is mixed with some other solvents in order to obtain well defined waves. The main disadvantage of this method is that the sensitivity is fairly decreased as the amount of the organic solvent used for the extraction is generally large and secondly the pH of the extract has to be readjusted in order to match the conditions with the standard. In the present paper a new method of extraction has been proposed in which the metal complex is extracted with melted naphthalene and separated from the aqueous phase by solidification and subsequent filtration or de-

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cantation. Since the extraction has been carried out at high temperature, the equilibrium in the two phases is attained rapidly; the complexes are extracted merely by contact with molten naphthalene and the main advantage is that a very small amount of the organic phase is required for the extraction which favors in getting well defined waves and also enhances the sensitivity; there is no need of readjusting the pH of the organic phase. In the present communication this technique was utilized for the extraction of cadmium-oxinate complex in melted naphthalene and the estimation of the element from naphthalene was made polarographically. The method is simple, rapid and accurate. The main advantage over spectrophotometric method is that only a few metal ions undergo reduction at a particular potential thus making the technique more selective without the use of masking agents.

EXPERIMENTAL

Reagents

Cadmium chloride solution was prepared by dissolving its G. R. sample in distilled water, standardised complexometrically.⁸⁾ The cadmium content in the stock solution was found to be 11.20 mg/ml. 0.1 M solution of oxine from G. R. sample was prepared by dissolving in 5 ml of glacial acetic acid and diluting to 100 ml with distilled water. G. R. samples of sodium perchlorate and perchloric acid were dissolved in water and dimethylformamide (DMF) respectively to make 2 M solution of each. Naphthalene and DMF used were also of G. R. grade and tested polarographically before use. For studying the effect of diverse ions, 1.0 g salt of the anions and 0.1 g salt of the cations were dissolved in water and made 100 ml in each case. pH values were adjusted using ammonia and acetic acid. Demineralized and twice distilled water was used wherever required.

Equipments

Polarograms in all instances were recorded at $25 \pm 0.5^\circ\text{C}$ with Yanagimoto polarograph P-8 with three electrode system. An H-type cell with fine porosity sintered glass disk between the two compartments was used. A saturated calomel electrode used as the reference electrode was connected to one compartment of the polarographic cell through potassium chloride-agar bridge. Dropping mercury electrode with drop time of 4.78 sec at a mercury head of 60 cm in DMF plus 0.1 M solution of the supporting electrolytes with open circuit was used. In each case the solution was deaerated by bubbling nitrogen before recording the polarogram. Hitachi pH-meter with glass electrode was used for measuring pH values.

Cadmium-Oxinate Standard

An aliquot of the cadmium chloride solution was taken in a beaker, precipitated with oxine solution according to Berg,⁹⁾ filtered through 45 μ milli-pore filter paper, washed with water, dissolved with DMF solution containing 2 drops of perchloric acid per 100 ml and made 100 ml in a volumetric flask with the DMF solution. This solution was used as a standard solution for establishing suitable conditions for the polarographic analysis.

General Procedure

An aliquot of cadmium chloride solution was taken in a 100 ml round bottom flask, to this solution added 1 ml of oxine solution, diluted to 30–40 ml with distilled water, adjusted the pH of this solution in the optimum range of 7–10, stoppered the flask, warmed in the water-bath at a temperature of about 60°C, added 2 g of naphthalene and again heated in the water-bath till naphthalene melted to form a separate liquid layer. The flask was taken out from the water-bath and stirred till naphthalene separated out as a solid mass. Once more the flask was heated to remelt the naphthalene, shaken vigorously and allowed to stand. Naphthalene was separated by filtration, dried in the folds of the filter papers, dissolved in DMF (by little warming), transferred to a 20 ml flask, added 1.0 ml of sodium perchlorate solution and 1.0 ml of perchloric acid solution, and made 20 ml with DMF, 10 ml of this solution was taken in the polarographic cell, deaerated with nitrogen for 3 min. and recorded the polarogram. In each case diffusion current was referred to the calibration curve.

Polarography of Cadmium-Oxinate

Preliminary experiments indicated that a well defined wave of cadmium-oxinate can be obtained in 0.1 M perchloric acid and 0.1 M sodium perchlorate solutions with $E_{\frac{1}{2}} = -0.63$ V *vs* S. C. E. (Fig. 1). Aqueous solution of sodium perchlorate and the DMF solution of perchloric acid were recommended as the stock solution of supporting electrolyte. Due to the limited solubility of sodium perchlorate in DMF and naphthalene in water, sodium perchlorate in aqueous and perchloric acid in DMF solution were preferred.

Effect of Naphthalene on the Polarogram of Cd-Oxinate

An aliquot of cadmium-oxinate solution (containing 56 μ g of Cd) was taken in

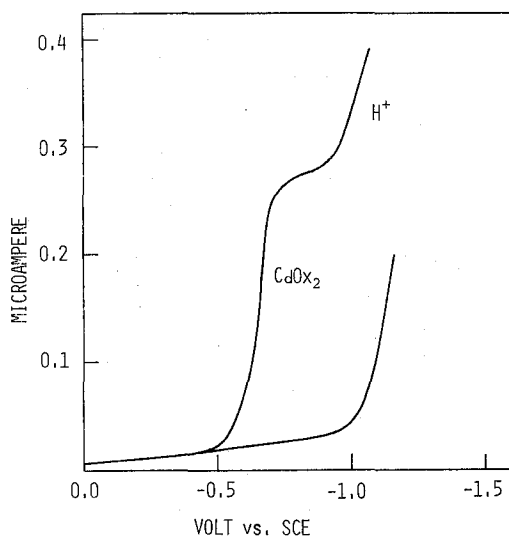


Fig. 1. Cadmium taken: 56.0 μ g, Naphthalene: 1.0g, Sodium perchlorate: 0.1 M, Perchloric acid: 0.1 M, Drop time: 4.78 sec, Recorder sensitivity: 3×10^{-9} A/mm, Mercury column height: 60 cm and Temperature: $25 \pm 0.5^\circ\text{C}$

Table I. Effect of Naphthalene on the Polarographic Wave of Cadmium-Oxinate
 Amount of Cadmium added = 56.0 μ g/10 ml
 Sodium perchlorate and Perchloric acid = 0.1 M each

Naphthalene added in g	i_d mm	$E_{1/2}$ in Volt (vs S.C.E.)	Remarks
0.00	83	-0.63	
0.30	83	-0.63	
0.60	83	-0.63	
0.90	83	-0.63	
1.20	83	-0.63	
1.50	82	-0.63	
1.75	76	-0.63	i_d started decreasing
2.00	73	-0.63	

the polarographic cell, added the supporting electrolyte similar to the general procedure and the amount of naphthalene was varied from 0.0–2.0 g by taking different volume of its 30% solution in DMF. Up to 1.50 g of naphthalene added, had no effect on the diffusion current as well as on $E_{1/2}$, but above this amount the diffusion current started decreasing. The effect is given in Table I.

Effect of Reagent on the Polarogram of Cd-Oxinate

Since all the polarograms had been recorded in the presence of 1 g of naphthalene, the effect of oxine was studied in the presence of 1 g of naphthalene. The amount of the reagent was varied from 0.0–150 mg by taking different volume of its 5% solution in DMF. Up to the amount of 100 mg, the reagent had no effect on the diffusion current as well as on the shape of the polarogram, but above this concentration, the upper plateau started distorting.

Effect of Water on the Polarogram of Cd-Oxinate

Polarograms were recorded in the presence of 1 g of naphthalene in each case and the amount of water was varied from 0.0–1.5 ml in different steps. It was observed

Table II. Effect of Water on the Polarographic Wave of Cadmium-Oxinate
 Naphthalene = 1.0 g
 Other conditions same as in Table I

Volume of Water added in ml/10ml	i_d in mm	$E_{1/2}$ in Volt (vs S.C.E.)	Remarks
0.0	83	-0.63	
0.1	83	-0.63	
0.2	83	-0.63	
0.4	83	-0.63	
0.6	81	-0.63	i_d begins to decrease
0.8	77	-0.63	
1.0	70	-0.63	
1.2	65	-0.63	
1.5	63	-0.63	precipitate appeared

Polarographic Trace Analysis of Cadmium and Lead

Table III. Dependence of Cd Wave Height on the Height of the Mercury Column

Cadmium wave height (i_d) mm	Mercury column height (mm)	$H^{\frac{1}{2}}$ of mercury column (mm) $^{\frac{1}{2}}$	$i_d/H^{\frac{1}{2}}$
47.0	280	16.740	2.807
50.0	330	18.165	2.748
53.0	380	19.493	2.719
57.0	430	20.736	2.751
60.0	480	21.908	2.740
65.0	580	24.083	2.700
68.0	630	25.099	2.711
71.0	680	26.076	2.724
73.0	730	27.018	2.704
74.0	780	27.928	2.651

that water up to 0.5 ml had no effect on diffusion current as well as on the shape of the polarogram, but above this amount, diffusion current started decreasing though $E_{\frac{1}{2}}$ remained constant. The effect is given in Table II.

The linear dependence of the limiting current on the square root of the height of the mercury column indicates that the rate of the reduction of cadmium-oxinate is diffusion controlled. (Table III) The plot of $\log i/(i_d-i)$ versus E gives a straight line with slope equal to -37 mV and intercept -0.63 V; *vs* S. C. E. this indicates that cadmium-oxinate is reduced slightly irreversibly, since the value of the slope is a little higher than the theoretical value of -30 mV for the two electron reduction. A number of polarograms were recorded in DMF, naphthalene, 0.1 M sodium perchlorate, 0.1 M

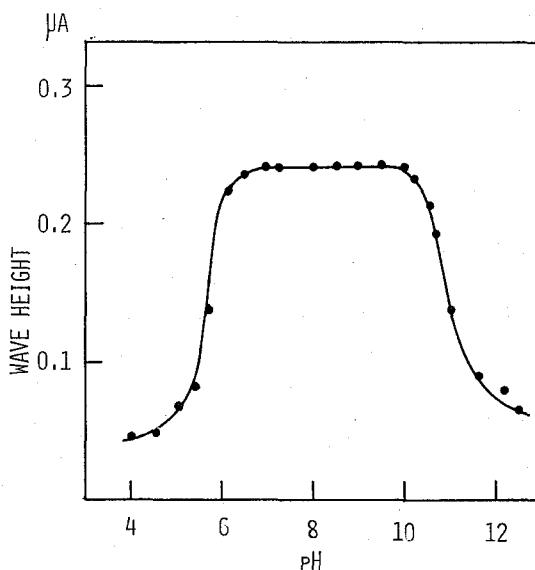


Fig. 2. Effect of pH on the Extraction of Cadmium
Amount of cadmium taken in each case: 112.0 μ g, Naphthalene taken for extraction in each case: 2.0g and Reagent used in each case: 1.0 ml of 0.1M solution in water-acetic acid mixture

perchloric acid and with different concentrations of cadmium-oxinate solution. The graph plotted between concentrations of cadmium-oxinate and diffusion currents gave a straight line in the concentration range of 0.0–112.0 μg per 10 ml of the solution. This fact indicates that the wave of cadmium-oxinate can be used for its quantitative determination under the conditions mentioned. The diffusion current constant I calculated from the Ilkovic equation $I = i_d / C m^{2/3} t^{1/6}$ is 2.389 which indicates that the method is equally sensitive as the usual polarographic methods in aqueous media. 5.60–201.60 μg of cadmium can be determined by this method with a standard deviation of 0.08 μg .

Effect of pH on the Extraction of Cadmium

Extractions were carried out by taking 112.0 μg of cadmium, 2 g of naphthalene, 1.0 ml of 0.1 M solution of the reagent and at different pH. It was found that the extraction was complete in the pH range of 7–10 as indicated by the Fig. 2.

Effect of the Reagent on the Extraction of Cadmium

As indicated in the effect of the reagent on the polarogram of cadmium-oxinate it is necessary to establish the minimum amount of the reagent required for the complete extraction. Extractions were carried out at a constant pH, amount of naphthalene, amount of cadmium and with different amount of the reagent. It was found that the extraction was complete down to 5 mg of the reagent, therefore in all the cases the extractions were carried out with 15 mg of the reagent.

Effect of Naphthalene on the Extraction of Cadmium

To establish the minimum amount of naphthalene, required for the complete extraction, extractions were carried out at a constant pH, amount of the reagent and amount of cadmium and with different amount of naphthalene. It was noted that the extraction was complete only when the amount of naphthalene was greater than 0.5 g, therefore in all the cases the extraction was carried out with 2 g of naphthalene for safe side.

Effect of the Aqueous Phase on the Extraction of Cadmium

Since the amount of the organic phase used for the extraction is very small as compared with the aqueous phase, it is necessary to observe the effect of the aqueous phase on the extraction. Extractions were carried out in the presence of 2 g of naphthalene, 112.0 μg of cadmium, 1.0 ml of the reagent, at a constant pH but at different volume of the aqueous phase. It was noted that more than 99% of cadmium was extracted when the volume of the aqueous phase was less than 300 ml, but above this volume of the aqueous phase the extraction became less quantitative. The effect is given in Table IV.

Effect of Diverse Ions on the Estimation of Cadmium

In general 100 mg salt of the anions and 1 mg salt of the cations were added individually in case of each extraction and the effect on the estimation was noted. Among all the ions examined, EDTA gave serious effect because cadmium was not extracted in its presence however, any other ions did not give serious effect in the estimation of cadmium. The results is given in Table V.

Polarographic Trace Analysis of Cadmium and Lead

Table IV. Effect of the Aqueous Phase on the Extraction of Cadmium
Amount of Cadmium taken = 112.0 μg
Naphthalene taken for extraction = 2.0 g
Reagent taken for extraction = 1.0 ml of 0.1 M solution
Sodium perchlorate and perchloric acid solution = 0.1 M each
Recorder sensitivity = 3×10^{-9} A/mm,

Volume of the aqueous phase ml	% of Cadmium Extracted
50	99.70
100	99.70
150	99.70
200	99.45
250	99.45
300	99.15
400	97.91
500	95.87

Table V. Effect of the Diverse Ions on the Determination of Cadmium

Salt added	Amount of ion added in mg	Amount of Cd found μg	Remarks
Sodium citrate	62.90	112.12	No extraction
Sodium phosphate	25.00	112.25	
Sodium borate	40.50	111.75	
Sodium azide	64.60	111.50	
Sodium flouride	45.20	112.00	
Sodium oxalate	66.60	111.50	
Di-sod-EDTA	79.90	—	
Potassium thiocyanate	59.70	111.50	
Sod-pot-tartrate	66.80	112.00	
Potassium chloride	47.60	112.00	
Potassium bromide	67.20	111.88	
Potassium iodide	76.50	111.75	
Palladdim chloride	00.60	111.50	
Uranyl acetate	00.56	112.25	
Lead nitrate	00.66	112.50	
Sodium tungstate	00.56	111.50	
Chromium nitrate	00.36	112.00	
Ferric chloride	00.20	111.80	
Copper sulphate	00.25	112.50	
Soddium vanadate	00.43	111.50	
Bismuth nitrate	00.43	112.50	
Thalous nitrate	00.76	112.00	
Silver nitrate	00.75	111.75	
Mercuric chloride	00.90	111.50	
Stanic chloride	00.42	112.50	
Sodium molybdate	00.39	112.50	

CONCLUSION

In comparison with the conventional liquid-liquid extraction, this technique is more rapid since the equilibria is established in few seconds due to high temperature. As filtration is involved, the phases can be more accurately separated and using very small amount of naphthalene, trace amount of metals can be concentrated through the extraction process. With further combination of the polarographic method to estimate the metal from the organic phase instead of using spectrophotometric method, made the technique more rapid, simple and selective which is obvious from Table V. A. C. polarographic and square wave polarographic methods were also tried, but the results were found to be unsatisfactory since the reagent acted as electro masking agent for cadmium and the height of the peaks were relatively small and almost constant at wide range of concentration.

SUMMARY

A rapid polarographic method has been developed for the direct estimation of cadmium extracted into the organic phase.

The Recommended Procedures Are as Follows

Cadmium was extracted as cadmium-oxinate with molten naphthalene in the pH range of 7–10; as the temperature was lowered, naphthalene was separated out as solid mass containing cadmium-oxinate, this solid mass was dissolved in DMF and the polarogram was recorded using 0.1 M sodium perchlorate and 0.1 M perchloric acid as the supporting electrolytes. Under these conditions, cadmium-oxinate gives a well defined wave with $E_{\frac{1}{2}} = -0.63$ V vs S. C. E. The relation between i_d and cadmium concentration was linear in the range of 0.0–112.0 $\mu\text{g}/10$ ml of the test solution. Metal ions which are expected to be reduced under the voltage range studied were examined, and none of them were found to interfere under these conditions. Among the ions studied only the interference of EDTA was noticed. The method is simple, selective, rapid and can be applied to the estimation down to 0.6 ppm with 10 ml sample, however, the sensitivity can be further raised with the increased sample size.

Part-2 Lead

The naphthalene extraction-polarographic method applied for the determination of lead is reported in this chapter. The extracted lead-8-quinolate is dissolved in dimethylformamide (DMF), a part of this solution was taken out, mixed with supporting electrolyte and recorded the polarogram. The interferences of various ions have been studied in details and the possible ways of masking has also been suggested. The procedure is rapid, sensitive, selective under suitable conditions and thus can be applied for the determination of lead in the various complex materials.

EXPERIMENTAL

Reagents

Lead nitrate solution was prepared by dissolving its G. R. sample in distilled water

in the presence of a few drops of nitric acid, standardized by known method¹⁰) and was found to contain 20.70 mg-Pb/ml. G. R. sample of 8-hydroxyquinoline (Oxine) was used in making 0.1 M solution in alcohol. 2 M solution of perchloric acid and pyridine were prepared from their G. R. samples in DMF and water respectively. Naphthalene and DMF were from G. R. samples and tested polarographically before use. To study the effect of diverse ions, 1.0 g salt of the anions and 0.1 g salt of the cations were dissolved in water and made 100 ml in each case. 5% solution of sodium cyanide, 20% of potassium thiocyanate and 10% of sodium-potassium tartrate were prepared from their G. R. samples in water. The pH of the solutions were controlled with potassium hydroxide and perchloric acid. Demineralized and twice distilled water was used wherever required. Polarograph, cell, pH-meter and the electrodes were the same as described in the previous chapter.

Lead-Oxinate Standard

An aliquot of lead nitrate solution was taken in a beaker, precipitated with oxine solution according to Hovorka,¹¹) filtered through 45 μ millipore filter paper, washed with cold water, dissolved in DMF and made 100 ml exactly. This solution was used as a standard solution for studying the polarographic behavior of lead-oxinate.

General Procedure

An aliquot of lead nitrate solution was taken in a 100 ml round bottom flask, added 1 ml of 0.1 M solution of the reagent, 2 ml of the tartrate solution, diluted to 25–35 ml with distilled water, adjusted the pH with potassium hydroxide solution,^{9–12}) stoppered the flask, warmed in the water-bath at a temperature of about 60°C, added 2 g of naphthalene, again heated in the water-bath till naphthalene melted and formed a separate liquid layer. This solution was stirred till naphthalene separated as a solid mass. Once more the flask was heated till the naphthalene remelted, shaken vigorously and allowed to stand. Naphthalene was separated by filtration, dried in the fold of filter papers, dissolved in DMF with little warming, transferred to a 10 ml flask, added 0.5 ml of pyridine solution, 0.5 ml of perchloric acid solution, and made 10 ml exactly. This solution was then transferred to the polarographic cell deaerated for 5 min. with nitrogen and recorded the polarogram.

Polarography of Lead-Oxinate in DMF

Preliminary experiments indicated that a well defined wave of lead-oxinate can be obtained in 0.1 M pyridine and 0.1 M perchloric acid. Aqueous solution of pyridine and DMF solution of perchloric acid have been preferred but there is no criteria, these solution can be interchanged *i.e.* DMF solution of pyridine and aqueous solution of perchloric acid but the pyridine solution must be added first and the perchloric acid next. Both electrolyte solutions can be made in water but it limits the use of naphthalene. On the other side when the solutions of both the electrolytes were prepared in DMF, the wave was not well defined.

Effect of Naphthalene on the Polarogram of Lead-Oxinate

A definite volume of lead-oxinate solution was taken (103.5 μ g of Pb) in the polarographic cell similar to the general procedure and the amount of naphthalene was varied from 0.0–2.7 g by taking different volume of its 30% solution in DMF. Naphthalene

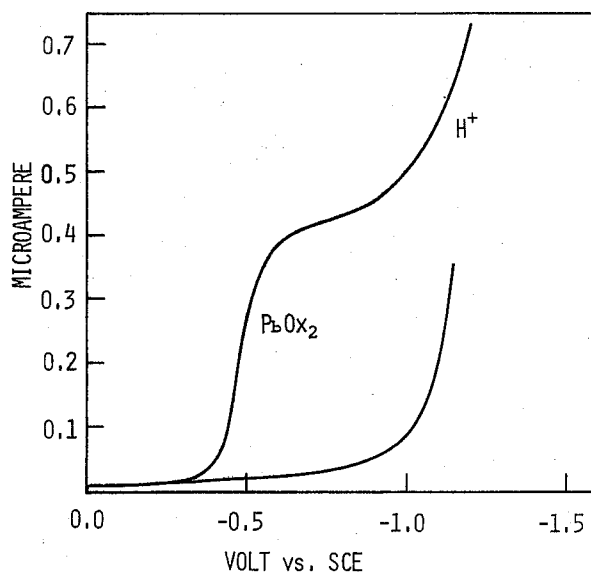


Fig. 3. Lead taken: 103.5 μ g, Naphthalene: 2.0 g, Pyridine: 0.1 M, Perchloric acid: 0.1 M, Drop time: 4.78 sec, Recorder sensitivity: 5×10^{-9} A/mm, Mercury column height: 60 cm and Temperature: $25 \pm 0.5^\circ\text{C}$.

has no effect on i_d up to an amount of 2.25 g, but above this amount i_d was slightly decreased.

Effect of Reagent on the Polarogram of Lead-Oxinate

As all polarograms has been recorded in the presence of 2 g of naphthalene, so the effect of oxin had been studied in the presence of 2 g of naphthalene. The amount of the reagent was varied from 0.0–150 mg by taking different volume of its 5% solution in DMF. It was observed that the reagent had no effect on i_d as well

Table VI. Effect of Water on the Polarographic Wave of Lead-Oxinate:

Amount of Lead taken = 103.5 μ g/10 ml

Naphthalene added = 2.0 g

Perchloric acid and Pyridine = 0.1 M each

Volume of Water added in ml/10 ml	i_d in mm	$E_{\frac{1}{2}}$ in Volt (vs S.C.E.)	Remarks
0.00	77.5	-0.47	
0.10	77.0	-0.47	
0.20	77.0	-0.47	
0.30	77.0	-0.47	
0.40	77.0	-0.46	$E_{\frac{1}{2}}$ shifted towards + i_d begins to decrease
0.50	76.5	-0.45	
0.70	75.0	-0.44	
0.80	69.1	-0.44	
1.00	60.0	-0.44	precipitate appeared

Table VII. Dependence of Pb Wave Height on the Height of the Mercury Column

Lead wave height (i_d) mm	Mercury column height (mm)	$H^{\frac{1}{2}}$ of mercury column (mm) $^{\frac{1}{2}}$	$i_d/H^{\frac{1}{2}}$
64.0	280	16.7400	3.822
75.0	380	19.4935	3.849
85.5	480	21.9089	3.859
93.0	580	24.0831	3.863
100.5	680	26.0768	3.855
107.5	780	27.9284	3.850

as on the shape of the polarogram, but $E_{\frac{1}{2}}$ was shifted slightly towards the negative direction ($E_{\frac{1}{2}}-0.47$ V to $E_{\frac{1}{2}}-0.48$ V).

Effect of Water on the Polarogram of Lead-Oxinate

Polarograms were recorded in the presence of 2 g of naphthalene in each case and the amount of water was varied from 0.0–1.0 ml in different steps. It was observed that water up to 0.4 ml had no effect on i_d but above this amount, i_d started decreasing. The effect is given in Table VI.

As already stated that lead-oxinate gives well defined wave in DMF in the presence of naphthalene, 0.1 M pyridine and 0.1 M perchloric acid. The linear dependence of the limiting current on the square root of the height of mercury column indicates that the reduction of lead-oxinate is a diffusion process. (Table VII) The plot of $\log i/(i_d-i)$ versus E gives a straight line with slope equal to 33 mV and intercepts -0.47 V *vs* SCE. This means that lead-oxinate is reduced reversibly with two electron change.

A number of polarograms in DMF, naphthalene, 0.1 M pyridine, 0.1 M perchloric acid and with different concentrations of lead-oxinate solution were drawn. The diffusion currents were measured by the extrapolation method. The graph plotted between concentrations of lead-oxinate and diffusion currents gave a straight line showing that the wave of lead-oxinate under these conditions can be used for its quantitative determination. The concentration range used for the calibration was 5.18–207.00 μ g of lead/10 ml of the solution. The diffusion current constant I calculated from the Ilkovic equation, $I=i_d/Cm^{2/3}t^{1/6}$ is 2.14 which indicates that the method is equally sensitive with the conventional polarographic method in the aqueous media. 10.35–207.00 μ g of lead can be determined by this method with standard deviation of 0.12 μ g.

Effect of pH on the Extraction of Lead

Preliminary experiments indicated that the extraction of lead is only complete in the presence of a weak complexing agent like tartrate as the formation constant of lead-oxinate and lead hydroxide are not far separated.¹²⁾ Thus the effect of pH was studied in the presence of tartrate ion (2 ml of 10% solution of sodium potassium tartrate was added in each case). Extractions were carried out by taking 103.5 μ g of lead, 2 g of naphthalene, 1 ml of 0.1 M solution of the reagent and 2 ml of tartrate solution at different pH. It was established that the favorable pH range for the complete extraction was 9–12 as indicated in Fig. 4.

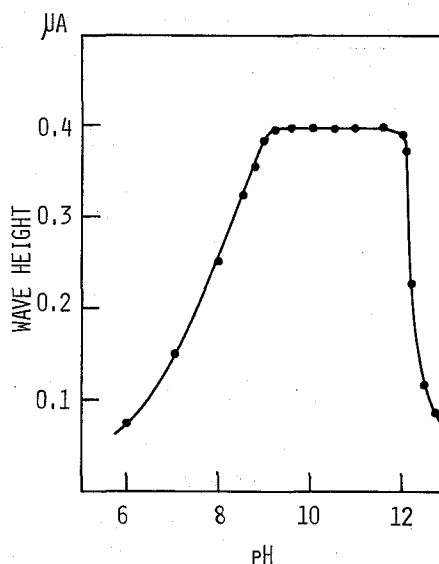


Fig. 4. Effect of pH on the Extraction of Lead

Amount of lead taken in each case: 103.5 μ g, Naphthalene taken in each case: 2.0 g, and Reagent used in each case: 1.0 ml of 0.1 M solution in alcohol.

Effect of the Reagent on the Extraction of Lead

In order to establish the minimum amount of the reagent required for the complete extraction, extractions were carried out at a constant pH, amount of naphthalene, amount of lead and different amount of the reagent. It has been found that the extraction is complete above 1.25 mg of the reagent, so in all the cases the extractions were carried out in the presence of 15 mg of the reagent.

Table VIII. Effect of the Aqueous Phase on the Extraction of Lead:

Amount of Lead taken = 103.5 μ g
 Naphthalene taken for extraction = 2.0 g
 Reagent taken for extraction = 1.0 ml of 0.1 M solution
 Perchloric acid and pyridine solutions = 0.1 M each
 Recorder sensitivity = 5×10^{-9} A/mm

Volume of the aqueous phase ml	% of Lead Extracted
25.0	99.76
50.0	99.32
100.0	99.32
150.0	96.50
200.0	82.00
250.0	60.00
300.0	52.00
350.0	40.00
400.0	28.00
500.0	28.00

Effect of Naphthalene on the Extraction of Lead

To establish the minimum amount of naphthalene required for the complete extraction, extractions were carried out at constant pH, amount of the reagent and lead. It has been noted that the extraction is only complete when the amount of amount of naphthalene used is greater than 0.75 g. So in all the cases the extractions were carried out with 2 g of naphthalene.

Effect of Aqueous Phase on the Extraction of Lead

Since the size of the organic phase used is so small as compared to the aqueous phase, it was necessary to observe the effect of the aqueous phase on the extraction of lead. Extractions were carried out in the presence of 2 g of naphthalene, 103.5 μg of lead and 1 ml of the reagent at constant pH with different volume of the aqueous phase. It has been found that the extraction is more than 99% when the volume of the aqueous phase is 100 ml but above this volume the extraction was considerably decreased. The effect is given in Table VIII.

Table IX. Effect of Diverse Ions on the Determination of Lead:
Conditions same as in Table VIII

Salt added	Amount of foreign Ion added in mg	Amount of Lead found in μg	Remarks
Sodium citrate	31.45	103.50	
Sodium oxalate	15.54	102.50	maximum amount tolerable
Sodium borate	20.20	102.75	
Sodium azide	32.30	103.75	
Sodium flouride	22.60	102.50	
Sodium thiosulphate	21.10	103.25	
Sodium phosphate	1.75	103.00	maximum amount tolerable
Di-sodium-EDTA	39.95	—	No extraction
Potassium thiocyanate	29.85	103.50	
Sod-pot-tartrate	33.40	103.75	
Potassium chloride	23.80	102.75	
Potassium bromide	33.60	103.25	
Potassium iodide	38.25	103.75	
Sodium tungstate	00.56	103.75	
Ferric chloride	00.20	104.00	
Copper nitrate	00.25	102.75	
Silver nitrate	00.75	103.50	
Sodium molybdate	00.39	103.00	
Thalious nitrate	00.76	104.00	
Bismuth nitrate	00.43	102.50	
Chromium nitrate	00.36	103.50	
Uranyl acetate	00.56	104.00	
Sodium vanadate	00.43	103.50	
Mercuric chloride	00.90	103.75	masked as cyanide
Palladium chloride	00.60	103.00	masked as cyanide
Cadmium chloride	00.51	102.50	masked as cyanide

Effect of Diverse Ions on the Estimation of Lead

Tests were made in the presence of 50 mg salt of the anions or 1 mg salt of the cations added individually in the extraction. It had been found that the results were slightly low in the presence of oxalate and largely in the presence of phosphate but the extraction became complete in both the cases when their amount was relatively decreased. The extraction was not possible in the presence of EDTA as the formation constant of EDTA chelate is higher than oxine chelate. Among the cations examined, Cd^{2+} , Pd^{2+} and Hg^{2+} interfere seriously but all these were masked by adding 10 ml of 5% sodium cyanide solution. The interference of mercury can also be eliminated by adding 20 ml of 20% potassium thiocyanate solution. Other ions have no effect on the estimation. The results are summarized in Table IX.

SUMMARY

A rapid polarographic method has been described for the direct estimation of lead from the organic phase after extraction. Lead has been extracted as oxinate by liquid-liquid extraction with molten naphthalene at high temperature in the pH range of 9–12. With the lowering of temperature, naphthalene separate out as a solid mass containing lead-oxinate, this solid mass is dissolved in DMF and the polarogram is recorded using 0.1 M pyridine perchlorate as the supporting electrolyte. Under these conditions lead gives a well defined wave with $E_{1/2} = -0.47 \text{ V vs S. C. E.}$ The relation between i_d and lead concentration is linear in the concentration range of 5.18–207.0 μg in 10 ml of the solution. Among the anions tested, EDTA interfered seriously while in case of cations, Cd^{2+} , Pd^{2+} and Hg^{2+} interfered but their interference could be eliminated by masking with cyanide ions. Other ions have no effect on the estimation. The method is simple, rapid, selective and sensitive; the estimation was made down to 1 ppm in the final solution and the sensitivity can be increased further by taking larger volume of the aqueous phase, and can be applied for the estimation of lead in natural and waste water and complex materials as well as alloys.

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